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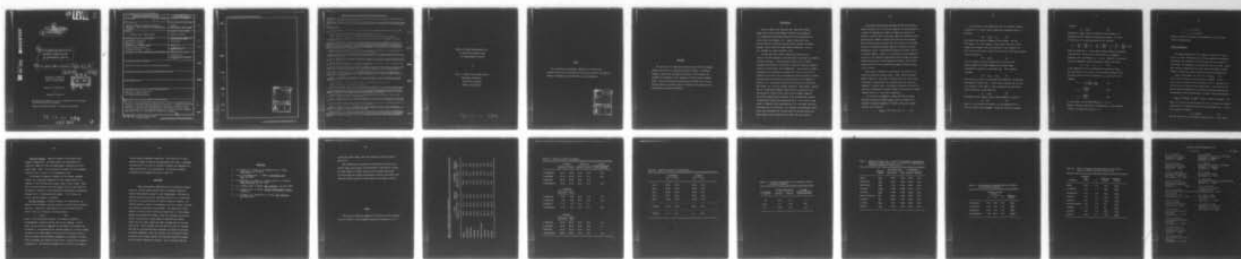   FEB 79   D L WINDSOR, M B DENTON   N00014-75-C-0513
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⑥ EMPIRICAL FORMULA DETERMINATION WITH AN INDUCTIVELY COUPLED PLASMA GAS CHROMATOGRAPHIC DETECTOR.

⑩ David L. Windsor and M. Bonner Denton

⑪ 1 Feb 79

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University of Arizona
Tucson, Arizona 85721

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The ability of the inductively-coupled plasma (ICP) gas chromatographic (GC) detector to determine empirical formulas is evaluated. Elemental compositions and empirical formulas of hydrocarbons and halogens are determined as the compounds are eluted from a chromatograph. The observed accuracy and precision are found to be of sufficient quality to indicate that the technique holds promise for the determination of empirical formulas.

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Empirical Formula Determination with

an Inductively Coupled Plasma

Gas Chromatographic Detector

by

David L. Windsor and M. Bonner Denton*

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79 02 21 073

Brief

The simultaneous multielement capabilities of inductively-coupled plasma emission spectrometry are used to determine the empirical formula of compounds eluted from from a gas chromatograph.

Abstract

The ability of the inductively-coupled plasma (ICP) gas chromatographic (GC) detector to determine empirical formulas is evaluated. Elemental compositions and empirical formulas of hydrocarbons and halogens are determined as the compounds are eluted from a chromatograph. The observed accuracy and precision are found to be of sufficient quality to indicate that the technique holds promise for the determination of empirical formulas.

Introduction

Previous studies have indicated that inductively-coupled
plasma atomic emission spectrometry (ICP-AES) can be employed
as a simultaneous multielement detector for the determination of
a wide variety of elements (1-3). Recent studies have shown
that the ICP can be used for the quantitative analysis of carbon,
hydrogen, boron, chlorine, sulfur iodine, phosphorous, silicon,
etc. contained in organic molecules (4,5).

The data from these studies suggest the possibility of
using the ICP-AES technique for the determination of empirical formulas
of organic molecules. This manuscript reports initial studies
evaluating the ability of the ICP-AES to determine empirical formulas
of species eluting from a gas chromatograph. Since empirical formula
determination is dependent on measuring the relative ratios of the
elemental constituents and not determining absolute quantities, factors
limiting quantitative delivery of known amounts of the compound in
question, i.e., limitations associated with quantitative injection,
peak shapes, etc., are not of major importance. Additionally, through
the use of high-speed computer controlled data acquisition, data
describing the relative atomic ratios of the elements composing
the eluting compound can be acquired as the concentration increases
to maximum peak height and subsequently falls. This yields a large
number of elemental ratio determinations for a wide range of analyte
concentrations at the detector. The computer can subsequently select
those ratio determinations falling within the observed linear res-
ponse range (4) and average these to obtain the best accuracy.

In previous investigations employing ICP-AES for analyzing organic molecules (4), the relative response of a given species in a variety of compounds was found to be much less sensitive to molecular structure than in the argon supported microwave excited plasma detector (MEPD), although some variations were observed. Such variations could seriously limit the ability of the ICP-AES detector to accurately determine empirical formulas if partial degradation results in preferential production of atomic species of certain elements. However, if a percentage of the compound in question is not completely degraded and passes through the plasma without producing any atomic degradation products, the relative atomic ratios will not be affected and empirical formula results will be correct.

Once empirical formulas are determined, the possibility of predicting molecular formulas exists. Under constant chromatographic conditions, the number of carbon atoms for a given class of molecule is proportional to a constant times the log of the component's retention time. The empirical formulas initially obtained can be employed to provide insight into selecting the proper constant value (i.e., the class of molecule).

If initially the assumption is made that when an organic compound of molecular formula $C_p H_q X_r$ enters the plasma it is thermally decomposed completely to atomic species, the thermal reaction can be given as:

$$C_p H_q X_r \xrightarrow{\quad \Delta \quad} pC + qH + rX \qquad (1)$$
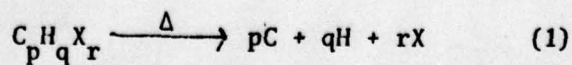
If the response versus weight curve for each element, produced by Reaction 1, is linear, then an analytical calibration curve of the form:

$$R_i^o = m_i w_i^o + b_i \qquad (2)$$

will describe the emission response of each element. For the ith element: R^o is the response, m the slope of the line, w^o the weight of the element, and b_i the intercept of the response axis. If b_i can be either made to equal zero or much less than $m_i w_i^o$, equation 2 can be reduced to:

$$R_i^o = m_i w_i^o \qquad (3)$$

The total weight of a given element (w_i^o) is the sum of the weight produced by an added compound (w_i) and the weight contributed by impurities in the argon (w_i'). Thus, equation 3 becomes:

$$R_i^o = m_i w_i + m_i w_i' \qquad (4)$$

The term $m_i w_i'$ in equation 4 represents the background and emission from impurity elements (R_i'). If this term is actually due to a constant impurity in the argon, it can be subtracted out and the net emission intensity is then given by:

$$R_i = m_i w_i \qquad (5)$$

The weight of each element, from an added compound, is given by:

$$w_i = P_i W \qquad (6)$$

where P_i is the fraction of element i in the compound and W is the total weight of the compound. Under this condition, equation

5 becomes:

$$R_i = m_i P_i W \qquad (7)$$

Assuming the response per unit weight for each element to be
independent of the compound containing the elements, the ratios
of the slopes of the working curves will be constants:

$$K_1 = \frac{m_c}{m_h} = \frac{R_c P_h}{R_h P_c} ; \quad K_2 = \frac{m_c}{m_x} = \frac{R_c P_x}{R_x P_c} ; \quad K_3 = \frac{m_h}{m_x} = \frac{R_h P_x}{R_x P_h} \qquad (8\text{-}10)$$

where the subscripts c, h and x denote carbon, hydrogen and element
X respectively. Equations 8-10 contain only two independent
equations since, for example, $K_3 = K_2/K_1$. Equation 11 constitutes
the third independent equation required to define the system:

$$P_c + P_h + P_x = 1 \qquad (11)$$

If one compound is used to determine the constants K_1 and K_2,
then the values of P_c, P_h and P_x for and unknown compound can be
determined from the emission responses (R_c, R_h and R_x) for the
compound:

$$P_c = \frac{R_c}{R_c + K_1 R_h + K_2 R_x} \qquad (12)$$

$$P_h = \frac{K_2 R_h P_c}{R_c} \qquad (13)$$

$$P_x = \frac{K_2 R_x P_c}{R_c} \qquad (14)$$

For the special case of hydrocarbons, $R_x = P_x = 0$.
However, problems would occur if recombination to form diatomics
occured to an appreciable extent, i.e.:

$$H + O \longrightarrow OH$$

$$C + O \longrightarrow CO \text{ etc.}$$
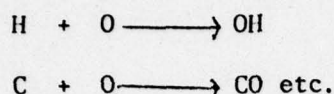
Previous studies (5) indicate that recombination is not a major source of interference.

Thermal Degradation

If thermal degradation is not complete, Equations 8-10 may or may not be valid, depending on the resulting decomposition products. Furthermore, the assumption that the response per unit weight for each element is independent of structure may also be invalid. Incomplete thermal decomposition may result from some molecules passing through or around the plasma discharge without any decomposition;

$$C_pH_qX_r \xrightarrow{\Delta} f[pC + qH + rX] + [1 - f]C_pH_qX_r \qquad (15)$$
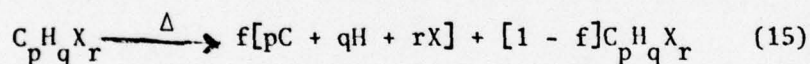
where f is the fraction of molecules not decomposed. In this case, W can be replaced by fW in Equations 6 and 7. Equations 8-10 and 12-14 are not altered by this substitution. The possibility of partial thermal decomposition of individual molecules producing non-stoichiometric atomic concentrations is a more serious consideration.

$$C_pH_qX_r \xrightarrow{\Delta} [f_1p]C + [f_2q]H + [f_3r]X + \text{molecular fragments} \qquad (16)$$
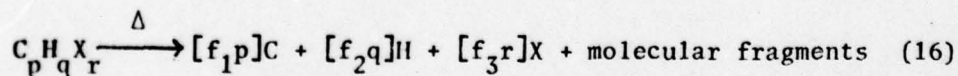
where f_1, f_2 and f_3 are the fractions of carbon, hydrogen and element X, respectively, are produced by partial thermal decomposition. In this case, equation 7 becomes:

$$R_1 = m_1P_1f_1W \qquad (17)$$

and the fractions f_1 are retained in equations 6-8. If this should

occur to any significant degree, equations 12-14 would no longer be valid.

It is the purpose of this manuscript to investigate which of these assumptions are valid and evaluate the actual performance of the ICP for the determination of empirical formulas.

Experimental

The experimental configuration employed consists of the R. F. supply, computer controlled data acquisition and gas chromatographic sampling system previously described (4,5). The torch is similar to the design of Windsor, et. al. (6), except that the internal diameter of the sample introduction tube has been reduced to 0.1 mm to decrease dead volume (5). All studies were performed with a single set of plasma operating conditions. Forward power of 800 watts at 27.12 MHz was utilized. A region 9 mm above the load coil was viewed. Coolant, plasma and sample argon were operated at 12, 0.5 and 0.9 L/min., respectively.

In addition to the previously described scanning optical system (4), a Jarrell-Ash (Waltham, Massachusetts) model 66-100 1.5 meter Paschen-Runge direct reader (200 μm entrance and 75 μm exit slits) equipped with high speed FET electrometers and a National Semiconductor (Santa Clara, California) model LF 13508 analog multiplexer is interfaced through a Burr-Brown (Tucson, Arizona) ADC 80-AG-10 analog to digital converter to a Hewlett-Packard (Palo Alto, California) 2116 C minicomputer equipped with 16 K of memory. The FET electrometers are

operated with a time constant of less than 100 µsec and sampled
sequentially for a given ratio value at a rate of 1.6 KHz providing
essentially simultaneous readout. The delay time between high-speed
scans of the monitored channels is software selectable based on a
crystal controlled real-time-clock. Typical peaks yielded 200 elemental
ratio determinations which were subsequently averaged to produce the
values shown in Tables I through VI.

The sampling system is a Varian (Walnut Creek, California) model
1520 gas chromatograph equipped with a model D2-1866 Automatic Linear
Temperature Programmer. The column employed is a 6 foot, 3.175 mm
O.D. column packed with 8 % carbowax 1540 on 80/100 mesh firebrick.
The output of the column is connected directly to a 1/57 mm Swagelok
"T". One branch of the "T" is the "makeup" argon (0.9 L/min) and the
third branch goes to the sample tube of the plasma torch. All reagents
were A. R. grade used without further purification.

Results and Discussion

In order to evaluate the accuracy and precision of the method
and determine which of the simplifying assumptions were warranted, the
hydrogen-carbon and carbon/hydrogen/halogen percentage composition for
a series of hydrocarbons and halogenated hydrocarbons were determined.
The data given in Tables I and II demonstrate close agreement between
theoretical and experimental values. Reproducibility data are given in
Tables III and IV.

<u>Empirical Formulas</u>. Empirical formulas are determined from
elemental compositions. For hydrocarbons, the experimental H/C
ratios are compared to those for hydrocarbons containing 20 or less
carbon atoms. Table V lists the empirical formula, for each compound,
whose H/C ratio is closest to the experimental value.

To determine the empirical formulas for the halogen compounds
studied, the percentage composition of each element found in the
compound is first divided by the atomic weight of that element. These
ratios are then adjusted so that the halogen ratio was one (Table VI).
The empirical formulas are then obtained by rounding off the carbon and
hydrogen ratios to the nearest whole number. In all cases, the
correct empirical formula is obtained.

<u>Molecular Formulas</u>. Molecular formulas, for hydrocarbons, are
deduced from experimental empirical formulas by utilizing the retention
time data. Approximate carbon numbers (n) were determined from re-
tention times (T_r) according to the relationship:

$$n \propto k \log T_r \qquad\qquad (18)$$

where k is an experimental constant. The constant k depends on
chromatographic conditions and the class of the compound. In this
study, the two classes of compounds are considered to be aromatic and
non-aromatic. To characterize the retention properites of the GC column,
the ratio of the carbon number to the log of the retention time for a
series of aromatic and non-aromatic compounds is determined. For each
class of compound, the average of these ratios is taken as the constant
in Equation 18. The observed constants are 11.7 and 22.7 for aromatic

and non-aromatic compounds respectively. The decision as to which constant to employ is based on the experimental H/C ratios. Compounds with ratios of 1.5 or less are classed as aromatic and compounds with ratios greater than 1.5 as non-aromatic. The molecular formulas determined by this method are listed in Table VII.

Conclusion

These investigations demonstrate that an inductively-coupled plasma can provide highly accurate relative elemental composition analysis when properly coupled to a gas chromatograph. The observed accuracy and precision for the compounds studied are at a sufficiently high level to allow calculation of reliable empirical formulas. The observed empirical formula can subsequently be used to choose a constant and estimate an approximate carbon number. Only approximate carbon numbers are needed since the molecular formula must be a whole number multiple of the empirical formula. While this technique provides the ability to analyze for a large number of elemental constituents, usable lines for atomic oxygen and atomic nitrogen have not yet been observed (4). Until suitable lines are found for these two elements, care must be exercised when these techniques are applied to mixtures of unknown components. While the relative ratios of measured atomic constituents will remain accurate, the calculated empirical formulas will not reflect elements not observed. Use of retention times for

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calculating carbon number under such conditions could also lead to gross error.

Even considering the limitations arising from the inability to measure oxygen and nitrogen, the high degree of quantitative accuracy and large number of elements which can be determined should make the ICP-GC empirical formula determination technique described by this manuscript highly valuable to both analytical and organic chemists.

Credit

Table I. Elemental analysis of hydrocarbons

	% Carbon			% Hydrogen		
	Theoretical	Found	Relative Difference (%)	Theoretical	Found	Relative Difference (%)
cumene	90.00	89.72	0.31	10.00	10.28	2.80
cyclohexene	87.80	87.94	0.16	12.20	12.06	1.15
ethylbenzene	90.57	90.57	0.00	9.43	9.43	0.00
n-heptane	84.00	83.92	0.10	16.00	16.08	0.50
isooctane	84.21	84.15	0.07	15.79	15.85	0.38
methylcyclohexane	85.71	85.72	0.01	14.29	14.28	0.07
1-pentene	85.71	85.98	0.32	14.29	14.02	1.89
o-xylene	90.67	90.67	0.00	9.43	9.43	0.00
m-xylene	90.57	90.48	0.10	9.43	9.52	0.95

Table II. Elemental analysis of halogens.

	% Carbon		Difference		Average Standard Deviation (parts/thousand)
	Theoretical	Found	Absolute	Relative	
1-iodobutane	26.10	25.86	0.24	0.92	12.3
2-iodobutane	26.10	26.40	0.30	1.15	10.9
iodobenzene	35.32	35.07	0.25	0.71	-
1-chlorobutane	51.90	51.81	0.09	0.17	2.8
	% Hydrogen				
	Theoretical	Found			
1-iodobutane	4.89	4.84	0.05	1.02	7.3
2-iodobutane	4.89	4.88	0.01	0.20	9.9
iodobenzene	2.47	2.31	0.16	6.5	-
1-chlorobutane	9.80	9.73	0.07	0.71	8.6
	% Halogen				
	Theoretical	Found			
1-iodobutane	69.00	69.31	0.31	0.45	1.4
2-iodobutane	69.00	68.72	0.28	0.41	1.4
iodobenzene	62.21	62.61	0.40	0.64	-
1-chlorobutane	38.30	38.46	0.16	0.42	4.9

Table III. Repetitive analysis of hydrocarbons.

| | Cyclohexene | | | m-Xylene | |
	% C	% H		% C	% H
Run 1	88.07	11.93		90.54	9.46
Run 2	87.98	12.02		90.63	9.37
Run 3	88.06	11.94		90.43	9.57
Run 4	87.76	12.24		90.37	9.63
Run 5	87.85	12.15		90.38	9.62
Average	87.94	12.06		90.47	9.52
$\bar{\sigma}$ (ppt)	1.5	11.2		1.2	11.8

Table IV. Precision and accuracy for the elemental analysis
of organic compounds.

% of Element in Compound	Average Difference %		Average Standard Deviation (parts/thousand)
	Absolute	Relative	
50	0.14	0.19	1.7
10-50	0.17	1.03	9.8
1-10	0.08	1.21	9.4

Table V. Empirical formulas for a variety of hydrocarbons studied whose hydrogen to carbon atomic ratio is closest to the experimentally determined hydrogen to carbon ratios.

	Empirical Formula	H/C Atomic Ratio		% Difference	
		Theoretical	Found	Absolute	Relative
cumene	C_3H_4	1.333	1.376	0.043	3.23
cyclohexene	C_3H_5	1.667	1.646	0.021	1.26
ethylbenzene	C_4H_5	1.250	1.249	0.001	0.08
n-heptane	C_7H_{16}	2.286	2.299	0.013	0.57
isooctane	C_4H_9	2.250	2.260	0.010	0.44
methylcyclohexane	CH_2	2.000	1.999	0.001	0.05
1-pentene	CH_2	2.000	1.957	0.043	2.15
o-xylene	C_4H_5	1.250	1.249	0.001	0.08
m-xylene	C_4H_5	1.250	1.263	0.013	1.04

Table VI. Experimentally determined Empirical formulas
for halogenated compounds.

| | Normalized Atomic Ratios | | | Empirical Formula |
	C	H	X	
1-iodobutane	3.94	8.86	1.00	C_4H_9I
2-iodobutane	4.06	9.00	1.00	C_4H_9I
iodobenzene	5.92	4.69	1.00	C_6H_5I
1-chlorobutane	3.98	8.97	1.00	C_4H_9Cl

Table VII. Molecular formulas determined from the experimental empirical formula data and retention times.

Compound	Retention Time (min)	nC	Empirical Formula	Molecular Formula
cumene	6.40	9.4	C_3H_4	C_9H_{12}
cyclohexene	2.10	7.3	C_3H_5	C_6H_{10}
ethylbenzene	5.45	8.6	C_4H_5	C_8H_{10}
n-heptane	1.95	6.6	C_7H_{16}	C_7H_{16}
isooctane	1.98	6.7	C_4H_9	C_8H_{18}
methylcyclohexane	2.00	6.8	CH_2	C_7H_{14}
1-pentane	1.75	5.5	CH_2	C_6H_{12}
o-xylene	6.85	9.8	C_4H_5	C_8H_{10}
m-xylene	5.55	8.7	C_4H_5	C_8H_{10}

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